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Patent:

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(54) HERBICIDAL SULFONYLUREAS, THE PREPARATION AND USE THEREOF

(54) SULFONYLURES HERBICIDES; LEUR PREPARATION ET LEUR UTILISATION

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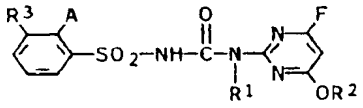
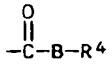
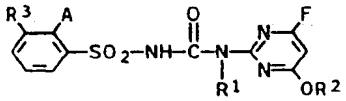


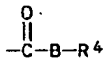


ABSTRACT OF THE DISCLOSURE: Substituted sulfonylureas of the general formula I



I,

where R^1 is hydrogen, C_1-C_3-alkyl, C_3-C_6-alkenyl or C_3-C_6-alkynyl; R^2 is C_1-C_4-alkyl; R^3 is hydrogen or halogen, and A is halogen or a radical



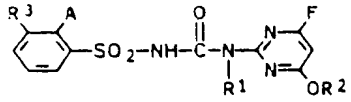
where B is oxygen or an alkylimino group

R^4 is hydrogen, C_1-C_6-alkyl which can carry up to three of the following: halogen, C_1-C_4-alkoxy, C_1-C_4-alkylthio, C_1-C_4-haloalkoxy, C_1-C_4-alkoxy-C_1-C_2-alkoxy, C_3-C_7-cycloalkyl and/or phenyl; C_5-C_7-cycloalkyl which can carry up to three C_1-C_4-alkyls; C_3-C_6-alkenyl or C_3-C_6-alkynyl, and R^5 is hydrogen, C_1-C_6-alkyl, or together with R^4 is a C_4-C_6-alkylene chain in which one methylene can be replaced by oxygen or C_1-C_4-alkylimino,

processes for their manufacture, and their use as herbicidal and growth-regulating agents.

Herbicidal sulfonylureas, the preparation and use thereof

The present invention relates to substituted sulfonylureas of the general formula I



I

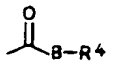
in which the substituents have the following meaning:

R^1 is hydrogen, C_1-C_3-alkyl, C_3-C_6-alkenyl or C_3-C_6-alkynyl;

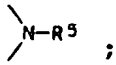
R^2 is C_1-C_4-alkyl;

R^3 is hydrogen or halogen and

A is halogen or



where B is oxygen or alkylimino



;

R^4 is hydrogen, C_1-C_6-alkyl which can carry up to three of the following: halogen, C_1-C_4-alkoxy, C_1-C_4-alkylthio, C_1-C_4-halogenoalkoxy, C_1-C_4-alkoxy-C_1-C_2-alkoxy, C_3-C_7-cycloalkyl and/or phenyl; C_5-C_7-cycloalkyl which can carry up to three C_1-C_4-alkyls; C_3-C_6-alkenyl or C_3-C_6-alkynyl and R^5 is hydrogen, C_1-C_6-alkyl, or together with R^4 is a C_4-C_6-alkylene chain in which one methylene can be replaced by oxygen or C_1-C_4-alkylimino.

The present invention furthermore relates to a process for the preparation of the compounds I as well as to the use thereof as herbicides.

US-A 4 547 215 discloses various herbicidal sulfonyl-pyrimidyl-ureas which are substituted in the pyrimidyl moiety by chlorine. However, these compounds are unsatisfactory because of the low selectivity for weeds and because of the relatively high application rates.

Hence the object of the invention was to find novel compounds from the sulfonyl-pyrimidyl-urea class with improved herbicidal properties.

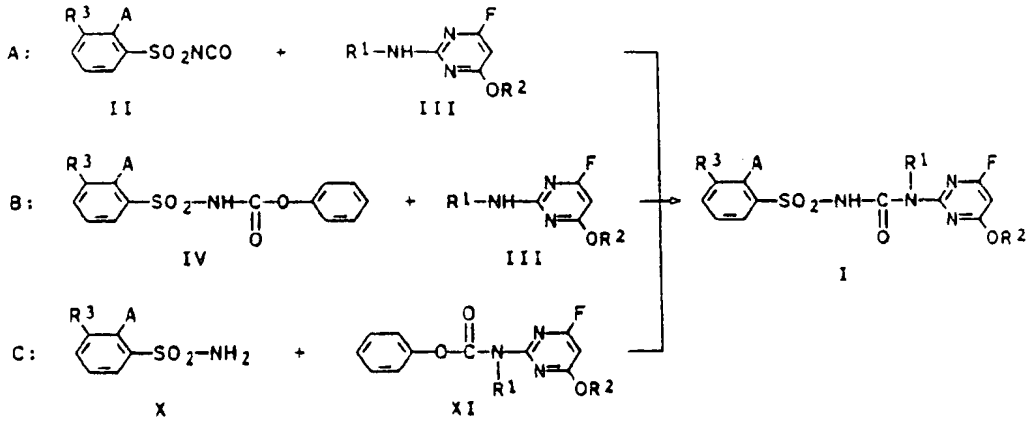
In accordance with this object, we have found the

sulfonylureas defined in the introduction.

We have furthermore found that the compounds I, as well as the alkali metal and alkaline earth metal salts thereof, have good selectivity for weeds in crops such as corn.

In addition, we have found some special chemical processes for preparing the compounds I. In particular, the synthesis of the precursor III entails, by comparison with the state of the art (J. Med. Chem. 6, (1963) 688; J. Chem. Soc. 6 (1970) 1280), less expense and has greater regioselectivity and thus a higher yield, which is a crucial advantage.

The sulfonylureas of the formula I according to the invention can be obtained in a variety of ways:



A: A sulfonyl isocyanate II is reacted in a conventional manner (EP-A 162 723) with approximately the stoichiometric amount of a 2-aminopyrimidine derivative III in an inert organic solvent at from 0 to 120°C, preferably 10 to 100°C. The reaction can be carried out under atmospheric or superatmospheric pressure (up to 50 bar), preferably under 1 to 5 bar, continuously or discontinuously.

Suitable solvents are listed in the above-mentioned literature.

B: An appropriate sulfonylcarbamate of the formula IV is reacted in a conventional manner (EP-A-162 723) with a 2-aminopyrimidine derivative III in an inert

organic solvent at from 0 to 120°C, preferably 10 to 100°C. It is possible to add bases such as tertiary amines, which increases the reaction rate and improves the quality of the product.

Examples of bases suitable for this purpose are tertiary amines such as pyridine, the picolines, 2,4- and 2,6-lutidine, 2,4,6-collidine, p-dimethylaminopyridine, 1,4-diazabicyclo[2.2.2]octane [DABCO] and 1,8-diazabicyclo[5.4.0]undec-7-ene.

The solvents which are expediently used are those specified in the literature and/or halogenated hydrocarbons such as dichloromethane and chlorobenzene, ethers such as diethyl ether, tetrahydrofuran and dioxane, acetonitrile, dimethylformamide and/or ethyl acetate in an amount of from 100 to 4000 % by weight, preferably 1000 to 2000 % by weight, based on the starting materials II, IV and X.

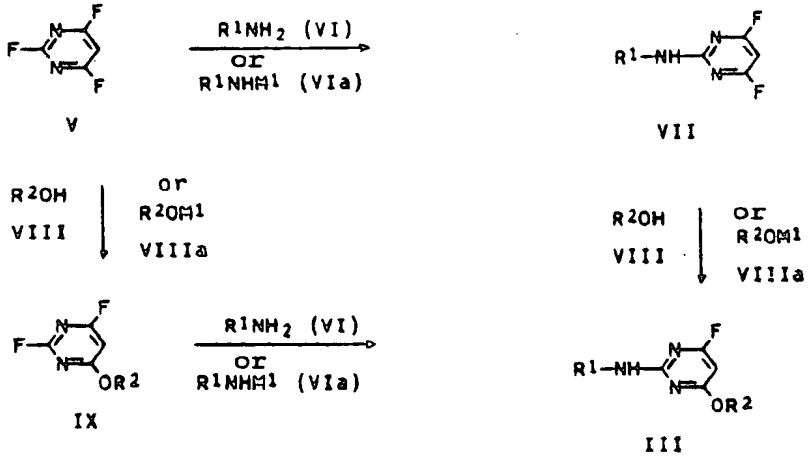
Of the intermediates III required according to the invention, 2-amino-4-ethoxy-6-fluoropyrimidine has been disclosed (J. Med. Chem. 6 (1963) 688). It has hitherto been necessary to prepare it in an elaborate manner from 2-amino-4,6-difluoropyrimidine and sodium ethylate in dry toluene with a change of the solvent and working up in ether, concentration and crystallization from a large volume of petroleum ether, the yield of crude product being, however, only 61 %.

It is even more difficult to obtain the 2-amino-4,6-difluoropyrimidine required as starting material, this having been obtained in 66 % yield by aminolysis of 2,4,6-trifluoropyrimidine in absolute ethanol followed by precipitations and washings of the residue and filtrate as well as a steam distillation to separate the isomers, other products being an isomeric 4-amino compound and hydrolysis products.

In a similar way, R.E. Banks et al. (J. Chem. Soc. 6 (1970) 1280) obtained, on aminolysis of trifluoropyrimidine in aqueous ammonia at 0°C, a mixture of isomers, with a yield of 53 % of the 2-amino and 26 % of the 4-amino compound.

In view of the unsolved problem with isomers, the yields and the reaction conditions, all the known processes are unsatisfactory in terms of simplicity and cost, especially on the industrial scale.

However, the intermediates III can be obtained in a considerably more advantageous manner during the preparation of the compounds according to the invention:



The compounds III are prepared in two independent reaction stages, the sequence of which can be inverted.

Thus, for example, 2,4,6-trifluoropyrimidine can be reacted in an aprotic polar solvent

a) with an amine VI, which can be in aqueous solution, in the presence or absence of a base and, if the reaction is carried out in two phases, in the presence of a phase-transfer catalyst or

b) with a metal amide VIa, in the absence or presence of a base, and, if the reaction is carried out in two phases, in the presence of a phase-transfer catalyst at from -80 to +20°C, after which the 2-aminopyrimidine derivative VII which has been obtained in this way is reacted without solvent or in the presence of an inert organic solvent

c) with an alcoholate VIII in the presence or absence of a base or

d) with an alcoholate VIIIa in the presence of the corresponding alcohol VIII

at from 0 to 140°C to give the aminopyrimidine III.

These reactions can be carried out under atmospheric or superatmospheric pressure (1 to 10 bar, preferably 1 to 5 bar), continuously or discontinuously.

M^1 in each of formulae VIa and VIIIa is an alkali metal cation such as lithium, sodium or potassium cation or the equivalent of an alkaline earth metal, such as magnesium, calcium or barium cation.

The following solvents are suitable for the reaction of 2,4,6-trifluoropyrimidine V with the amine R^1NH_2 (VI) to give VII:

ethers such as methyl tert.-butyl ether, diethyl ether, ethyl propyl ether, n-butyl ethyl ether, di-n-butyl ether, diisobutyl ether, diisoamyl ether, diisopropyl ether, cyclohexyl methyl ether, tetrahydrofuran, 1,2-dimethoxyethane, diethylene glycol dimethyl ether and anisole; chlorinated hydrocarbons such as 1,1,2,2-tetrachloroethane, 1,1-dichloroethylene, chlorobenzene, 1,2-dichlorobenzene and 1-chloronaphthalene as well as corresponding mixtures.

The solvent is expediently used in an amount of from 100 to 2000 % by weight, preferably 500 to 1500 % by weight, based on the starting material V.

It is advantageous to use as acid acceptor an excess of amine or the alkali metal or alkaline earth metal salt thereof. The amine is advantageously added in twice the equivalent amount, or up to 15 % above or below this, based on the starting material V, within 1 to 2 hours, to a mixture of starting material V in one of the abovementioned solvents at from -80 to 20°C, preferably -30 to -10°C, and the mixture is then stirred for up to one hour where appropriate and then allowed to warm to 25°C for the working out.

When the primary amine R^1NH_2 (VI, $R^1 \neq H$) is employed as aqueous solution, it is expedient to add to the reaction solution a phase-transfer catalyst.

Suitable for this purpose are, for example, crown ethers such as 15-crown-5 or 15-crown-6 and corresponding benzo-fused derivatives such as dibenzo-18-crown-6, polyethylene glycol dialkyl ethers of the type

(n = 5 to 7 and V and W, independently of one another, C_1-C_4-alkyl) as well as quaternary ammonium salts such as benzyltriethylammonium chloride, tetrabutylammonium iodide, tetrabutylammonium hydroxide and tetrabutylammonium bisulfate.

In this case the reaction is preferably carried out at from -15 to 20°C with addition of from 0.002 to 0.02 mol-equivalents of catalyst.

Reaction of starting materials VII and VIII is expediently carried out in excess alcohol VIII as solvent. Where appropriate, an alkali metal alcoholate VIIIa is added, in an equivalent amount or up to 5 % above or below this, based on the starting material VII, to a suspension of the starting material VII in 5 to 20 times the amount by weight of alcohol VIII as solvent, based on starting material VII, within up to one hour at from 20 to 80°C. The reaction is then completed by stirring at from 0 to 140°C, preferably 20 to 100°C, for 1/2 to 8 hours.

Examples of basic compounds which can be used are lithium, sodium, potassium, calcium, barium and magnesium in the form of their alcoholates; however, also suitable are organic bases such as trimethylamine, triethylamine, N-ethyldiisopropylamine, triisopropylamine, N,N-dimethylaniline, N,N-dimethylcyclohexylamine, N-methylpyrrolidine, pyridine, quinoline, α,β or γ-picoline, 2,4- and 2,6-lutidine and triethylenediamine.

When the reaction sequence is reversed, 2,4,6-trifluoropyrimidine (V) is reacted in the first stage either with an alcohol VIII or with its salt VIIIa to give the pyrimidine derivative IX which is then derivatized with an amine VI or its salt VIa to give the aminopyrimidine derivative III.

These reactions are carried out in the same solvents and using the same acid acceptors and same ratios of amounts as in the conditions described above.

The temperature for the reaction of V with the alcohol VIII or its salt VIIIa is from -20 to 140°C, preferably from 0 to 100°C, and for the reaction of IX with an amine VI or its salt VIa is from -40 to 100°C, preferably from -20 to +20°C.

The aminopyrimidines III are isolated by the methods of working up described in the literature.

Compared with the state of the art, the process according to the invention provides the compounds I in a more straightforward and economic manner with better yields and purity in all steps.

C: A sulfonamide of the formula X is reacted in a conventional manner (EP A 141 777) with approximately the stoichiometric amount of a phenyl carbamate XI in an inert organic solvent at from 0 to 120°C, preferably 20 to 100°C. The reaction can be carried out under atmospheric or superatmospheric pressure (up to 50 bar), preferably under 1 to 5 bar, continuously or discontinuously.

Examples of suitable solvents, besides those listed in the literature cited above, are nitrated hydrocarbons such as nitroethane and nitrobenzene, nitriles such as acetonitrile and benzonitrile, esters such as ethyl acetate, amides such as dimethylformamide and/or ketones such as acetone.

The reaction is preferably carried out in ethyl acetate as solvent and with pyridine or one of the abovementioned tertiary amines as base.

The sulfonamides required as starting materials of the formula IV can be prepared from 6-halogenoanthranilic esters by the Meerwein reaction and subsequent reaction with ammonia.

Compounds of the formula I in which R^4 is hydrogen are obtained by hydrolysis of esters of the formula I in which R^4 is C_1-C_6-alkyl. The hydrolysis is carried out with not less than twice the amount of a base, such as sodium or potassium hydroxide, expediently in a mixed solvent containing 2 to 8 times the amount of methanol and 10 to 40 times the amount of water, based on the

weight of the appropriate ester of the formula I, at from 30 to 80°C for from 1 to 20 hours. The sulfonamide carboxylic acids of the formula I are precipitated by acidification.

With regard to the biological activity, preferred compounds of the formula I are those in which the substituents have the following meanings:

R^1 is hydrogen and methyl,

R^2 is methyl, ethyl, n-propyl and isopropyl,

R^3 is hydrogen, fluorine, chlorine and bromine,

A is chlorine, carboxyl and aminocarbonyl,

R^4 is alkyl such as methyl, ethyl, n-propyl and isopropyl, alkenyl such as allyl, methallyl, crotyl and but-1-en-3-yl,

alkynyl such as propargyl, but-1-yn-3-yl and but-2-ynyl, halogenoalkyl such as 2-chloroethyl, 2-chloro-n-propyl, 3-chloro-n-propyl, 1-chloro-2-butyl, 2-chloro-iso-butyl, 4-chloro-n-butyl, chloro-tert.-butyl, 3-chloro-2-propyl and 2,2,2-trifluoroethyl,

alkoxyalkyl such as 2-methoxyethyl, 2-ethoxyethyl, 3-methoxy-n-propyl, 2-methoxy-n-propyl, 3-methoxy-n-butyl, 1-methoxy-2-butyl, methoxy-tert.-butyl, ethoxy-tert.-butyl, 2-methoxy-n-butyl, 4-methoxy-n-butyl, 2-ethoxy-n-propyl, 1-methoxy-2-propyl, 2-ethoxy-1-butyl and 4-ethoxy-n-butyl,

alkoxyalkoxyalkyl such as 2-methoxy-ethoxy-methyl, 2-(ethoxy)-ethoxy-methyl, 2-(propoxy)-ethoxy-methyl, 2-methoxy-ethoxy-ethyl, 2-(ethoxy)-ethoxy-ethyl and 2-(methoxy-methoxy)-ethyl,

halogenoalkoxyalkyl such as 2-(β-chloroethoxy)ethyl, 3-(β-chloroethoxy)-n-propyl and 3-(γ-chloro-n-propoxy)-n-propyl,

cycloalkyl such as cyclopentyl and cyclohexyl,

R^5 is hydrogen,

alkyl such as methyl, ethyl, n-propyl, isopropyl and n-butyl,

or together with R^4 is tetramethylene, pentamethylene, hexamethylene, ethyleneoxyethylene and ethylene-N-methyliminoethylene.

Examples of suitable salts of the compounds of the formula I are agriculturally useful salts, for instance alkali metal salts such as potassium and sodium salts; alkaline earth metal salts such as calcium, magnesium and barium salts; manganese, copper, zinc and iron salts, and ammonium, phosphonium, sulfonium and sulfoxonium salts, e.g., ammonium salts, tetraalkylammonium salts, benzyltrialkylammonium salts, trialkylsulfonium salts and trialkylsulfoxonium salts.

The novel herbicidal and growth-regulating agents I, or agents containing them, may be applied for instance in the form of directly sprayable solutions, powders, suspensions (including high-percentage aqueous, oily or other suspensions), dispersions, emulsions, oil dispersions, pastes, dusts, broadcasting agents, or granules by spraying, atomizing, dusting, broadcasting or watering. The forms of application depend entirely on the purpose for which the agents are being used, but they must ensure as fine a distribution of the active ingredients according to the invention as possible.

The compounds I are generally suitable for the manufacture of solutions, emulsions, pastes and oil dispersions to be sprayed direct. Suitable inert additives are mineral oil fractions of medium to high boiling point, such as kerosene or diesel oil, further coal-tar oils, and oils of vegetable or animal origin, aliphatic, cyclic and aromatic hydrocarbons such as benzene, toluene, xylene, paraffin, tetrahydronaphthalene, alkylated naphthalenes and their derivatives such as methanol, ethanol, propanol, butanol, chloroform, carbon tetrachloride, cyclohexanol, cyclohexanone, chlorobenzene, isophorone, and strongly polar solvents such as N,N-dimethylformamide, dimethyl sulfoxide, N-methylpyrrolidone and water.

Aqueous formulations may be prepared from emulsion concentrates, pastes, dispersions, wettable powders or water-dispersible granules by adding water. To prepare emulsions, pastes and oil dispersions the ingredients as such or dissolved in an oil or solvent may be homogenized in water by means of wetting or dispersing agents, adherents or emulsifiers. Concentrates which are suitable for dilution with water may be prepared from active ingredient, wetting agent, adherent, emulsifying or dispersing agent and possibly solvent or oil.

Examples of surfactants are: alkali metal, alkaline earth metal and ammonium salts of ligninsulfonic acid, naphthalenesulfonic acids, phenolsulfonic acids, alkylaryl sulfonates, alkyl sulfates, and alkyl sulfonates, alkali metal and alkaline earth metal salts of dibutylnaphthalenesulfonic acid, lauryl ether sulfate, fatty alcohol sulfates, alkali metal and alkaline earth metal salts of fatty acids, salts of

sulfated hexadecanols, heptadecanols, and octadecanols, salts of sulfated fatty alcohol glycol ethers, condensation products of sulfonated naphthalene and naphthalene derivatives with formaldehyde, condensation products of naphthalene or naphthalenesulfonic acids with phenol and formaldehyde, polyoxyethylene octylphenol ethers, ethoxylated isooctyl phenol, ethoxylated octylphenol and ethoxylated nonylphenol, alkylphenol polyglycol ethers, tributylphenyl polyglycol ethers, alkylaryl polyether alcohols, isotridecyl alcohol, fatty alcohol ethylene oxide condensates, ethoxylated castor oil, polyoxyethylene alkyl ethers, ethoxylated polyoxypropylene, lauryl alcohol polyglycol ether acetal, sorbitol esters, lignin, sulfite waste liquors and methyl cellulose.

Powders, dusts and broadcasting agents may be prepared by mixing or grinding the active ingredients with a solid carrier.

Granules, e.g., coated, impregnated or homogeneous granules, may be prepared by bonding the active ingredients to solid carriers. Examples of solid carriers are mineral earths such as silicic acid, silica gels, silicates, talc, kaolin, attapulgus clay, limestone, lime, chalk, bole, loess, clay, dolomite, diatomaceous earth, calcium sulfate, magnesium sulfate, magnesium oxide, ground plastics, fertilizers such as ammonium sulfate, ammonium phosphate, ammonium nitrate, and ureas, and vegetable products such as grain flours, bark meal, wood meal, and nutshell meal, cellulosic powders, etc.

The formulations contain from 0.1 to 95, and preferably 0.5 to 90, % by weight of active ingredient. The active ingredients are employed in a purity of from 90 to 100, preferably from 95 to 100, % (according to the NMR spectrum).

The compounds I according to the invention may be formulated for instance as follows:

I. 90 parts by weight of compound no. 1.010 is mixed with 10 parts by weight of N-methyl-alpha-pyrrolidone. A mixture is obtained which is suitable for application in the form of very fine drops.

II. 20 parts by weight of compound no. 1.001 is dissolved in a mixture consisting of 80 parts by weight of xylene, 10 parts by weight of the adduct of 8 to 10 moles of ethylene oxide and 1 mole of oleic acid-N-monoethanolamide, 5 parts by weight of the calcium salt of dodecylbenzenesulfonic acid, and 5 parts by weight of the adduct of 40 moles of ethylene oxide and 1 mole of castor oil. By pouring the solution into 100,000 parts by weight of water and uniformly distributing it therein, an aqueous dispersion is obtained containing 0.02% by weight of the active ingredient.

III. 20 parts by weight of compound no. 1.002 is dissolved in a mixture consisting of 40 parts by weight of cyclohexanone, 30 parts by weight of isobutanol, 20 parts by weight of the adduct of 7 moles of ethylene oxide and 1 mole of isooctylphenol, and 10 parts by weight of the adduct of 40 moles of ethylene oxide and 1 mole of castor oil. By pouring the solution into 100,000 parts by weight of water and finely distributing it therein, an aqueous dispersion is obtained containing 0.02% by weight of the active ingredient.

IV. 20 parts by weight of compound no. 2.006 is dissolved in a mixture consisting of 25 parts by weight of cyclohexanol, 65 parts by weight of a mineral oil fraction having a boiling point between 210 and 280°C, and 10 parts by weight of the adduct of 40 moles of ethylene oxide and 1 mole of castor oil. By pouring the solution into 100,000 parts by weight of water and uniformly distributing it therein, an aqueous dispersion is obtained containing 0.02% by weight of the active ingredient.

V. 20 parts by weight of compound no. 1.009 is well mixed with 3 parts by weight of the sodium salt of diisobutylnaphthalene-alpha-sulfonic acid, 17 parts by weight of the sodium salt of a lignin-sulfonic acid obtained from a sulfite waste liquor, and 60 parts by weight of powdered silica gel, and triturated in a hammer mill. By uniformly distributing the mixture in 20,000 parts by weight of water, a spray liquor is obtained containing 0.1% by weight of the active ingredient.

VI. 3 parts by weight of compound no. 1.058 is intimately mixed with 97 parts by weight of particulate kaolin. A dust is obtained containing 3% by weight of the active ingredient.

VII. 30 parts by weight of compound no. 1.059 is intimately mixed with a mixture consisting of 92 parts by weight of powdered silica gel and 8 parts by weight of paraffin oil which has been sprayed onto the surface of this silica gel. A formulation of the active ingredient is obtained having good adherence.

VIII. 20 parts by weight of compound no. 2.004 is intimately mixed with 2 parts of the calcium salt of dodecylbenzenesulfonic acid, 8 parts of a fatty alcohol polyglycol ether, 2 parts of the sodium salt of a phenolsulfonic acid-urea-formaldehyde condensate and 68 parts of a paraffinic mineral oil. A stable oily dispersion is obtained.

IX. 90 parts by weight of compound no. 2.001 is mixed with 10 parts by weight of N-methyl-alpha-pyrrolidone. A mixture is obtained which is suitable for application in the form of very fine drops.

X. 20 parts by weight of compound no. 1.009 is dissolved in a mixture consisting of 80 parts by weight of xylene, 10 parts by weight of the adduct of 8 to 10 moles of ethylene oxide and 1 mole of oleic acid-N-monoethanolamide, 5 parts by weight of the calcium salt of dodecylbenzenesulfonic acid, and 5 parts by weight of the adduct of 40 moles of ethylene oxide and 1 mole of castor oil. By pouring the solution into 100,000 parts by weight of water and uniformly distributing it therein, an aqueous dispersion is obtained containing 0.02% by weight of the active ingredient.

XI. 20 parts by weight of compound no. 1.001 is dissolved in a mixture consisting of 40 parts by weight of cyclohexanone, 30 parts by weight of isobutanol, 20 parts by weight of the adduct of 7 moles of ethylene oxide and 1 mole of isooctylphenol, and 10 parts by weight of the adduct of 40 moles of ethylene oxide and 1 mole of castor oil. By pouring the solution into 100,000 parts by weight of water and finely distributing it therein, an aqueous dispersion is obtained containing 0.02% by weight of the active ingredient.

XII. 20 parts by weight of compound no. 2.007 is dissolved in a mixture consisting of 25 parts by weight of cyclohexanol, 65 parts by weight of a mineral oil fraction having a boiling point between 210 and 280°C, and 10 parts by weight of the adduct of 40 moles of ethylene oxide and 1 mole of castor oil. By pouring the solution into 100,000 parts by weight of water and uniformly distributing it therein, an aqueous dispersion is obtained containing 0.02% by weight of the active ingredient.

XIII. 20 parts by weight of compound no. 3.001 is well mixed with 3 parts by weight of the sodium salt of diisobutylnaphthalene-alpha-sulfonic acid, 17 parts by weight of the sodium salt of a lignin-sulfonic acid obtained from a sulfite waste liquor, and 60 parts by weight of powdered silica gel, and triturated in a hammer mill. By uniformly distributing the mixture in 20,000 parts by weight of water, a spray liquor is obtained containing 0.1% by weight of the active ingredient.

XIV. 3 parts by weight of compound no. 1.059 is intimately mixed with 97 parts by weight of particulate kaolin. A dust is obtained containing 3% by weight of the active ingredient.

XV. 30 parts by weight of compound no. 1.009 is intimately mixed with a mixture consisting of 92 parts by weight of powdered silica gel and 8 parts by weight of paraffin oil which has been sprayed onto the surface of this silica gel. A formulation of the active ingredient is obtained having good adherence.

XVI. 20 parts by weight of compound no. 1.001 is intimately mixed with 2 parts of the calcium salt of dodecylbenzenesulfonic acid, 8 parts of a fatty alcohol polyglycol ether, 2 parts of the sodium salt of a phenol-sulfonic acid-urea-formaldehyde condensate and 68 parts of a paraffinic mineral oil. A stable oily dispersion is obtained.

The herbicidal or growth-regulating active ingredients, or agents containing them, may be applied pre-or postemergence. If certain crop plants tolerate the active ingredients less well, application techniques may be used in which the herbicidal agents are sprayed from suitable equipment in such a manner that the leaves of sensitive crop plants are if possible not touched, and the agents reach the soil or the unwanted plants growing beneath the crop plants (post-directed, lay-by treatment).

The application rates for the herbicidal use of the active ingredients depend on the objective to be achieved, the time of the year, the plants to be combated and their growth stage, and are from 0.001 to 3.0, preferably 0.01 to 1, kg of active ingredient per hectare.

The compounds of the formula I may exercise a variety of influences on practically all plant development stages, and are therefore used as growth regulators. The diversity of action of growth regulators depends especially on

a) the type and variety of plant;
b) the time applied, with reference to the development stage of the plants and the time of the year;
c) the place and method of application (seed treatment, soil treatment, or application to foliage);
d) climatic factors, e.g., average temperature, amount of precipitate, sunshine and duration;
e) soil conditions (including fertilization);
f) the formulation of the active ingredient; and
g) the concentration at which the active ingredient is applied.

A description of some of the various possibilities of using the growth regulators according to the invention in agriculture and horticulture is given below.

A. Vegetative plant growth can be inhibited to a considerable extent, a fact which is manifested particularly in a reduction in plant height. The treated plants thus have a compact habit; furthermore, the leaf color is darker.

Of advantage in practice is for example the reduction in grass growth on roadsides, hedges, canal embankments and on areas such as parks, sportsgrounds, fruit orchards, lawns and airfields, thus reducing expensive and time-consuming mowing.

A further feature of economic interest is the increase in the rigor of crops which tend to lodge, such as cereals, Indian corn, sunflowers and soybeans. The shortening and strengthening of the stem thus caused reduces or eliminates the danger of lodging under unfavorable weather conditions.

The use of growth regulators is also important for inhibiting plant height and changing the time of ripening in cotton. It is thus possible for this important crop to be harvested completely mechanically.

Pruning costs can be saved in fruit and other trees. Furthermore, growth regulators can break up the alternate bearing of fruit trees.

Growth regulators may also increase or inhibit lateral branching. This is of interest when, for instance in tobacco plants, it is desired to inhibit the formation of lateral shoots (suckers) in favor of leaf development.

With the growth-regulating compounds, it is possible for instance in winter rape to considerably increase the resistance to freeze injury. On the one hand, upward growth and the development of a too luxuriant (and thus particularly frost-susceptible) leaf or plant mass are inhibited; on the other, the young rape plants are kept, in spite of favorable growth conditions, in the vegetative development stage before winter frosts begin. The danger of freeze injury is thus eliminated in plants which tend to lose prematurely their inhibition to bloom and pass into the generative phase. In other crops, too, e.g., winter cereals, it is advantageous if the plants are well tillered in the fall as a result of treatment with the compounds according to the invention, but enter winter with not too lush a growth. This is a preventive measure against increased susceptibility to freeze injury and - because of the relatively low leaf or plant mass - attack by various (especially fungus) diseases. The inhibition of vegetative growth also makes closer planting possible in numerous crops, which means an increase in yield, based on the area cropped.

B. Better yields both of plant parts and plant materials may be obtained with the novel agents. It is thus for instance possible to induce increased formation of buds, blossom, leaves, fruit, seed grains,

roots and tubers, to increase the sugar content of sugarbeets, sugarcane and citrus fruit, to raise the protein content of cereals and soybeans, and to stimulate the increased formation of latex in rubber trees.

The compounds of the formula I may raise the yield by influencing plant metabolism or by promoting or inhibiting vegetative and/or generative plant growth.

C. It is also possible with growth regulators to shorten or lengthen growth stages and to accelerate or retard the ripening process in plant parts either before or after harvesting.

A factor of economic interest is for example the facilitation of harvesting made possible by a chemical, temporally concentrated loosening (abscission) of the adherence of stalks to the branches of citrus fruit, olive trees, and other kinds of pomes, drupes and indehiscent fruit. The same mechanism, i.e., promotion of the formation of separation layers between fruit or leaf and stem of the plant, is also essential for a readily controllable defoliation of crop plants, e.g., cotton.

D. Further, transpiration in crop plants may be reduced with growth regulators. This is particularly important for plants growing in agricultural areas which are expensive to irrigate, e.g., in arid or semi-arid areas. Irrigation frequency can be reduced by using the compounds according to the invention, making for lower costs. As a result of the use of growth regulators, the water available can be better utilized, because, inter alia,

- the size of the stomata opening is reduced;
- a thicker epidermis and cuticle are formed;
- penetration of the soil by the roots is improved;
- the micro-climate in the stand is favorably influenced by the more compact growth.

The active ingredients of the formula I to be used in accordance with the invention may be applied not only to the seed (as a disinfectant), but also to the soil, i.e., via the roots, and - the method particularly preferred - to the foliage by spraying.

As a result of the good crop plant tolerance, the application rates may vary within wide limits.

In view of the number of application methods possible, the herbicidal and growth-regulating agents according to the invention, or agents containing them, may be used in a further large number of crops for removing unwanted plants.

To increase the spectrum of action and to achieve synergistic effects, the compounds I according to the invention may be mixed and applied together with numerous representatives of other herbicidal or growth-regulating active ingredient groups. Examples of suitable components are diazines, 4H-3,1-benzoxazine derivatives, benzothiadiazinones, 2,6-dinitroanilines, N-phenylcarbamates, thiolcarbamates, halocarboxylic acids, triazines, amides, ureas, diphenyl ethers, triazinones, uracils, benzofuran derivatives, cyclohexane-1,3-dione derivatives, quinolinecarboxylic acid derivatives, aryloxy- or heteroaryloxy-phenoxypropionic acids and salts, esters and amides thereof, etc.

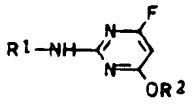
It may also be useful to apply the compounds I, either alone or in combination with other herbicides, in admixture with other crop protection agents, e.g., agents for combating pests or phytopathogenic fungi or bacteria. The compounds may also be mixed with solutions of mineral salts used to remedy nutritional or trace element deficiencies. Non-phytotoxic oils and oil concentrates may also be added.

Synthesis examples

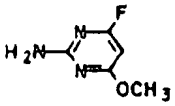
The procedures given in the examples which follow have been used with appropriate modification of the starting compounds to obtain further compounds of the formula I; the resulting compounds are listed with physical data in the tables which follow; compounds without these data can be synthesized from the appropriate substances in a similar manner. On the basis of their close structural relations to the compounds which have been prepared and investigated, they are expected to have similar effects.

Synthesis examples

1. Preparation of the intermediates III



1.1 2-Amino-6-fluoro-4-methoxypyrimidine (variant a)



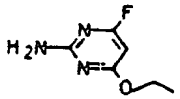
a) 2-amino-4,6-difluoropyrimidine

69.7 g (4.1 mol) of liquid ammonia were added at -30 to -20°C to a stirred mixture of 250 g (1,865 mol) of 2,4,6-trifluoropyrimidine in 3.3 l of diethyl ether within one hour. For the working up, the reaction mixture was allowed to warm to 25°C and the precipitate was filtered off. Washing with ether, stirring in water, renewed filtration and drying resulted in 203 g (83 % of theory) of the title compound of melting point 214-216°C. Concentration of the ether filtrate to about 1/3 of its volume allowed a further 20 g (8 % of theory) of the title compound of melting point 193-196°C to be isolated as a 1:1 mixture with the isomeric 4-amino compound.

b) 2-Amino-6-fluoro-4-methoxypyrimidine

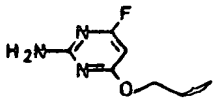
27 g of 30 % strength sodium methylate (0.15 mol) were added to a stirred suspension of 19.7 g (0.15 mol) of 2-amino-4,6-difluoropyrimidine in 250 ml of absolute methanol at 65°C within 20 minutes. The reaction solution was stirred under reflux for 5 hours and then cooled to 25°C, and the precipitate was removed, washed with a little methanol and then stirred in water. Filtration, washing with water and drying resulted in 16 g (74 % of theory) of the title compound of melting point 172°C. Concentration of the filtrate, washing with methanol and subsequently with water resulted in isolation of a further 3 g (14 % of theory) of the title compound of melting point 161-169°C.

1.2 2-Amino-4-ethoxy-6-fluoropyrimidine



A solution of 25.2 g (0.3 mol) of potassium ethylate in 200 ml of absolute ethanol was added to a stirred suspension of 39.3 g (0.3 mol) of 2-amino-4,6-difluoropyrimidine (1.1a) in 150 ml of absolute ethanol at 78°C within 40 minutes. The mixture was stirred under reflux for 5 hours and then cooled, and the solvent was removed under reduced pressure. The residue was stirred with water, filtered off, washed with water and dried. 39 g (83 % of theory) of the title compound of melting point 121-123°C were obtained (cf. Lit. J. Med. Chem. 6 (1963) 688; 61 % yield of crude product; melting point after recrystallization: 120.5-123°C).

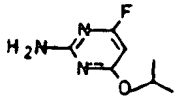
1.3 2-Amino-6-fluoro-4-propyloxypyrimidine



29.4 g (0.3 mol) of potassium propylate were reacted in a similar manner to 1.2 with 39.3 g (0.3 mol)

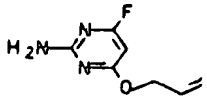
of 2-amino-4,6-difluoropyrimidine (1.1a) in a total of 400 ml of n-propanol. The solvent was removed from the reaction mixture under reduced pressure, and the residue was washed with petroleum ether. It was subsequently stirred in water, filtered off, washed and dried, resulting in 36.1 g (70 % of theory) of the title compound of melting point 63-66°C.

1.4 2-Amino-6-fluoro-4-isopropyloxypyrimidine



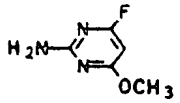
29.4 g (0.3 mol) of potassium isopropylate were reacted in a similar manner to 1.2 with 39.3 g (0.3 mol) of 2-amino-4,6-difluoropyrimidine (1.1a) in a total of 400 ml of isopropanol. Working up, washing with petroleum ether and water in the usual manner resulted in 38.5 g (75 % of theory) of the title compound of melting point 66-68°C.

1.5 4-Allyloxy-2-amino-6-fluoropyrimidine



1.14 g (0.0382 mol) of 80 % sodium hydride (emulsion in linseed oil) were added under a nitrogen atmosphere to 70 ml of allyl alcohol at 25°C. The mixture was stirred at 40°C for 20 minutes and then 6.0 g (0.0382 mol) of 2-amino-4,6-difluoropyrimidine (1.1a) were added to the clear solution, and the mixture was then stirred at 97°C for 1.5 hours. For the working up, the excess alcohol was removed by distillation under reduced pressure, the resulting residue was taken up in methylene chloride, and the solution was washed with water, dried over magnesium sulfate and then the solvent was removed. The resulting viscous oil crystallized on trituration with n-pentane. Filtration, washing with water and drying resulted in 4.6 g (71.2 % of theory) of the title compound of melting point 62-66°C.

1.6 2-Amino-6-fluoro-4-methoxypyrimidine (variant b)



a) 2,4-Difluoro-6-methoxypyrimidine

335.8 g (1.865 mol) of 30 % strength sodium methylate (in methanol) were added to a mixture of 250 g (1.865 mol) of 2,4,6-trifluoropyrimidine in 1.4 l of methanol at -20°C within 45 minutes, and the mixture was stirred at this temperature for a further 30 minutes. The reaction mixture was subsequently allowed to warm to 25°C and then concentrated to about 1/3 of its volume.

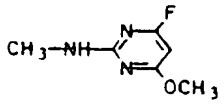
The mixture obtained in this way was partitioned between diethyl ether and water, and the organic phase was dried over magnesium sulfate and concentrated. Distillation (1.1 m column, 3 mm V-shaped packing) resulted in 141.6 g (52 % of theory) of the title compound of boiling point 144-145°C.

Distillation of the distillation residue without a column resulted in 114.4 g (42 % of theory) of 4,6-difluoro-2-methoxypyrimidine of boiling point 157-161°C.

b) 2-Amino-6-fluoro-4-methoxypyrimidine

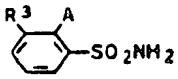
13.6 g (0.8 mol) of ammonia in 30 ml of methyl tert.-butyl ether were added at -20 to -10°C to a stirred mixture of 52 g (0.356 mol) of 2,4-difluoro-6-methoxypyrimidine in 300 ml of methyl tert.-butyl ether within 20 minutes. After a further 2 hours at -15° and 3 hours at 25°C, the precipitate was filtered off with suction, washed with methyl tert.-butyl ether, stirred with water, filtered off, washed again and subsequently dried, resulting in 36.1 g (71 % of theory) of the title compound of melting point 171-173°C.

1.7 4-Fluoro-6-methoxy-2-methylaminopyrimidine

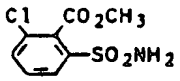


46.8 g of a 40 % strength solution of methylamine in water (0.605 mol) were added at 0 to 2°C to a stirred mixture of 41.9 g (0.287 mol) of 2,4-difluoro-6-methoxypyrimidine (1.6a) and a spatula-tip of triethylbenzylammonium chloride (phase-transfer catalyst) in 100 ml of methyl tert.-butyl ether within 30 minutes. After 1 hour at 0°C and 3 hours at 25°C, the organic phase was separated off, washed with water and concentrated under reduced pressure. The residue was stirred with pentane, resulting in 39.9 g (88 % of theory) of 4-fluoro-6-methoxy-2-methylaminopyrimidine of melting point 78-80°C.

2. Preparation of intermediates X



2.1 Methyl 2-aminosulfonyl-6-chlorobenzoate



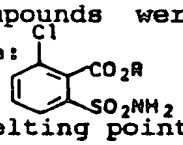
a) 4-Chloro-1,2-benzoisothiazol-3-one 1,1-dioxide

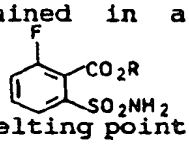
504 g (2.02 mol) of methyl 6-chloro-2-aminosulfonylbenzoate were added a little at a time to a solution of 80 g (2.0 mol) of sodium hydroxide in 2.5 l of water, during which the temperature rose from 25°C to 50°C. After 30 minutes at this temperature, the mixture was cooled to 25°C and extracted with methyl t-butyl ether, and the aqueous phase was stirred into 2 N hydrochloric acid. The precipitate was isolated, washed with water and dried. 330 g (75.8 % of theory) of the title compound of melting point 210-212°C were obtained.

b) Methyl 2-aminosulfonyl-6-chlorobenzoate

93 g (0.427 mol) of 4-chloro-1,2-benzoisothiazol-3-one 1,1-dioxide were suspended in 0.8 l of methanol and stirred under reflux, while passing in gaseous hydrogen chloride, for 3 hours. Cooling to 20°C, filtration with suction and drying resulted in 60 g (56.3 % of theory) of the title compound of melting point 152-153°C. Concentration of the filtrate under reduced pressure and trituration of the residue with methyl tert.-butyl ether, renewed filtration and drying resulted in 42 g (39.4 % of theory) of a second fraction of this compound, of melting point 144-149°C.

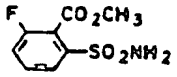
The following compounds were obtained in a similar manner, for example:





R	Melting point (°C)	Melting point (°C)
C_2H_5	97-101	129-131
$n\text{-}C_3H_7$	111-113	104-107
$i\text{-}C_3H_7$	145-147	84- 87
$CH_2CH{=}CH_2$	105-108	
CH_2CH_2Cl	130-134	109-110
$CH_2CH_2OCH_3$	102-104	135-136
$CH_2CH_2OCH_2CH_2Cl$	124-126	

2.2 Methyl 2-aminosulfonyl-6-fluorobenzoate



a) Methyl 2-chlorosulfonyl-6-fluorobenzoate

108 g (0.639 mol) of methyl 6-fluoroanthranilate and 45 g of sodium nitrite in 106 ml of water were added separately but simultaneously at 5°C with stirring to 250 ml of concentrated hydrochloric acid within 1 hour in such a way that the ester component was present in excess. After the reaction mixture had been stirred at

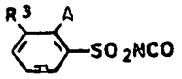
5 to 8°C for 20 minutes it was poured all at once into a prepared solution of 53 g of sulfur dioxide, 1.7 g of copper(II) chloride in a little water in 200 ml of 1,2-dichloroethane and then stirred for 10 minutes. The mixture was slowly heated to 50°C and, while passing in 46 g of sulfur dioxide, stirred for 1 1/2 hours. It was then cooled to 20°C and 5.5 g of chlorine were passed in within 20 minutes while stirring. After stirring for 20 minutes, the organic phase was separated off, washed with water and dried. 105 g (65 % of theory) of the title compound were obtained as a brownish oil in this way.

b) Methyl 2-aminosulfonyl-6-fluorobenzoate

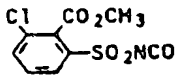
42.5 g of gaseous ammonia were passed at 20 to 23°C into a stirred mixture of 252.5 g (1 mol) of methyl 2-chlorosulfonyl-6-fluorobenzoate in 700 ml of anhydrous tetrahydrofuran. After the mixture had been stirred at 25°C for 1 hour, the precipitate was filtered off with suction, dissolved in water and extracted once with ethyl acetate. Acidification of the aqueous phase with concentrated hydrochloric acid resulted in 8.8 g (4.4 % of theory) of 4-fluoro-1,2-benzoisothiazol-3-one 1,1-dioxide of melting point 210-212°C.

The tetrahydrofuran filtrate was concentrated, and the residue was washed with water, filtered off, washed with diethyl ether, again filtered off and dried. 186 g (79.8 % of theory) of the title compound of melting point 155-159°C were obtained.

3. Preparation of intermediates II



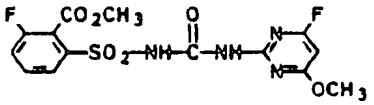
3.1 3-Chloro-2-methoxycarbonylbenzenesulfonyl isocyanate



100 g (0.4 mol) of methyl 6-chloro-2-aminosulfonylbenzoate were suspended in 300 ml of 1,2-dichloroethane and, while stirring, 123 g (1.03 mol) of thionyl chloride were added, and the mixture was slowly heated to reflux. After the mixture had been stirred under reflux for 5 hours it was cooled to 55°C, 1.5 ml of pyridine were added and, while passing in phosgene, the mixture was again heated to reflux. After gas had been passed in for 4 hours, the reaction mixture was concentrated under reduced pressure and ventilated with nitrogen. The remaining oil (105 g, 95.2 % of theory) was employed for the next stage without further purification.

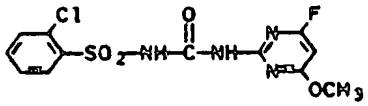
4. Preparation of active ingredients I

4.1 Methyl 6-fluoro-2-[N-(4-fluoro-6-methoxy-2-pyrimidinyl)aminocarbonylaminosulfonyl]benzoate



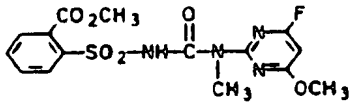
4.3 g (0.03 mol) of 3-fluoro-2-methoxycarbonylbenzenesulfonyl isocyanate in 15 ml of 1,2-dichloroethane were added at 25°C to a stirred suspension of 4.3 g (0.03 mol) of 2-amino-4-fluoro-6-methoxypyrimidine (1.1/1.6) in 70 ml of 1,2-dichloroethane within 15 minutes, and the mixture was stirred at 25°C for 12 hours. The precipitate was filtered off with suction, stirred first with 1 N hydrochloric acid, washed with water, then stirred with diethyl ether, filtered off with suction, washed and dried, resulting in 8.1 g (67 % of theory) of the title compound of melting point 203°C (decomposition) (active ingredient example 2.001).

4.2 1-Chloro-2-[N-(4-fluoro-6-methoxy-2-pyrimidinyl)-aminocarbonylaminosulfonyl]benzene



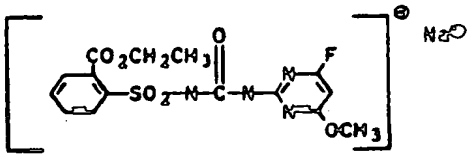
10.9 g (0.05 mol) of chlorobenzene-2-sulfonyl-isocyanate in 10 ml of 1,2-dichloroethane were added at 25°C to a stirred suspension of 7.15 g (0.05 mol) of 2-amino-4-fluoro-6-methoxypyrimidine (1.1/1.6) in 150 ml of 1,2-dichloroethane within 20 minutes, and the mixture was stirred for 8 hours. The reaction mixture was concentrated under reduced pressure, and the residue was stirred with methyl tert.-butyl ether, filtered off and washed. It was then stirred with 2 N hydrochloric acid, filtered off, washed with water and dried, resulting in 8.6 g (47.7 % of theory) of title compound of melting point 148-151°C (active ingredient example 3.001).

4.3 Methyl 2-[N-(4-fluoro-6-methoxy-2-pyrimidinyl)-N-methylaminocarbonylaminosulfonyl]benzoate



6.3 g (0.04 mol) of the compound 1.7 were introduced into 80 ml of 1,2-dichloroethane and, while stirring at 25°C, 9.6 g (0.04 mol) of 2-methoxycarbonyl-benzenesulfonyl isocyanate were added within 5 minutes. The reaction mixture was stirred at 25°C for 12 hours and then concentrated under reduced pressure. The residue was treated in the usual way with 1:1 diethyl ether/petroleum ether and with 1 N hydrochloric acid and with water. Drying resulted in 10.4 g (65 % of theory) of the title compound of melting point 148-150°C (active ingredient example 1.002).

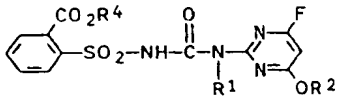
4.4 Sodium salt of ethyl 2-[N-(4-fluoro-6-methoxy-2-pyrimidinyl)aminocarbonylaminosulfonyl]benzoate



4.2 g (0.0109 mol) of ethyl 2-[N-(4-fluoro-6-methoxy-2-pyrimidinyl)aminocarbonylaminosulfonyl]benzoate (active ingredient example 1.009) were suspended in 80 ml

of methanol and, at 25°C, 1.9 g (0.0109 mol) of 30 % strength sodium methylate solution in methanol were added, and the mixture was stirred for 10 minutes. The solvent was removed by distillation under reduced pressure, resulting in 4.4 g (99.1 % of theory) of the title compound of melting point 175°C (decomposition) (active ingredient example 1.009 sodium salt).

Table 1

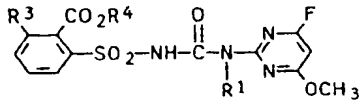


No.	R1	R2	R4	mp. (°C)
1.001	H	CH_3	CH_3	186-188
1.002	CH_3	CH_3	CH_3	148-150
1.003	H	CH_2CH_3	CH_3	169-170
1.004	CH_3	CH_2CH_3	CH_3	
1.005	H	$(CH_2)_2CH_3$	CH_3	156-158
1.006	CH_3	$(CH_2)_2CH_3$	CH_3	
1.007	H	$CH(CH_3)_2$	CH_3	134-135
1.008	CH_3	$CH(CH_3)_2$	CH_3	
1.009	H	CH_3	CH_2CH_3	165-168 175 [sodium salt]
1.010	CH_3	CH_3	CH_2CH_3	141-146
1.011	H	CH_3	$(CH_2)_2CH_3$	143-147
1.012	CH_3	CH_3	$(CH_2)_2CH_3$	
1.013	H	CH_3	$CH(CH_3)_2$	172-175
1.014	CH_3	CH_3	$CH(CH_3)_2$	
1.015	H	CH_3	$CH_2CH=CH_2$	
1.016	CH_3	CH_3	$CH_2CH=CH_2$	
1.017	H	CH_3	$CH_2C\equiv CH$	
1.018	CH_3	CH_3	$CH_2C\equiv CH$	
1.019	H	CH_3	$CH_2CH=CHCH_3$	
1.020	CH_3	CH_3	$CH_2CH=CHCH_3$	
1.021	H	CH_3	$CH_2C\equiv CCH_3$	
1.022	CH_3	CH_3	$CH_2C\equiv CCH_3$	
1.023	H	CH_3	$CH_2C(CH_3)=CH_2$	
1.024	CH_3	CH_3	$CH_2C(CH_3)=CH_2$	
1.025	H	CH_3	$(CH_2)_2Cl$	168-170
1.026	CH_3	CH_3	$(CH_2)_2Cl$	
1.027	H	CH_3	$(CH_2)_2OCH_3$	154-156
1.028	CH_3	CH_3	$(CH_2)_2OCH_3$	
1.029	H	CH_3	$(CH_2)_2O(CH_2)_2OCH_3$	
1.030	CH_3	CH_3	$(CH_2)_2O(CH_2)_2OCH_3$	
1.031	H	CH_3	$CH_2O(CH_2)_2OCH_2CH_3$	
1.032	CH_3	CH_3	$CH_2O(CH_2)_2OCH_2CH_3$	

Table 1 (contd.)

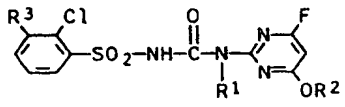
No.	R1	R2	R4	mp. (°C)
1.033	H	CH_3	CH_2CF_3	
1.034	CH_3	CH_3	CH_2CF_3	
1.035	H	CH_3	$C(CH_3)_2CH_2OCH_3$	
1.036	CH_3	CH_3	$C(CH_3)_2CH_2OCH_3$	
1.037	H	CH_3	$CH_2O(CH_2)_2OCH_3$	
1.038	CH_3	CH_3	$CH_2O(CH_2)_2OCH_3$	
1.039	H	CH_3	cyclopentyl	
1.040	CH_3	CH_3	cyclopentyl	
1.041	H	CH_3	cyclohexyl	
1.042	CH_3	CH_3	cyclohexyl	
1.043	H	CH_3	$(CH_2)_2SCH_3$	
1.044	CH_3	CH_3	$(CH_2)_2SCH_3$	
1.045	H	CH_3	$(CH_2)_2OCH_2CF_3$	
1.046	CH_3	CH_3	$(CH_2)_2OCH_2CF_3$	
1.047	H	CH_3	$CH_2C_6H_5$	
1.048	CH_3	CH_3	$CH_2C_6H_5$	
1.049	H	CH_3	$(CH_2)_3CH_3$	
1.050	CH_3	CH_3	$(CH_2)_3CH_3$	
1.051	H	CH_3	$CH_2CH(CH_3)_2$	
1.052	CH_3	CH_3	$CH_2CH(CH_3)_2$	
1.053	H	CH_3	$C(CH_3)_3$	
1.054	CH_3	CH_3	$C(CH_3)_3$	
1.055	H	CH_3	$CH(CH_3)CH_2CH_3$	
1.056	CH_3	CH_3	$CH(CH_3)CH_2CH_3$	
1.057	H	CH_3	$(CH_2)_2OCH_3$	142 (decomp.) [sodium salt]
1.058	H	CH_3	$(CH_2)_2Cl$	152 (decomp.) [sodium salt]
1.059	H	CH_3	CH_3	144 (decomp.) [sodium salt]
1.060	H	CH_3	CH_3	164 (decomp.) [sodium salt]
1.061	H	CH_3	$CH(CH_3)_2$	184 (decomp.) [sodium salt]
1.062	H	CH_3	$(CH_2)_2CH_3$	186 (decomp.) [sodium salt]

Table 2



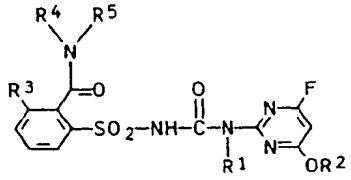
No.	R^1	R^3	R^4	mp. (°C)
2.001	H	F	CH_3	203 (decomp.)
2.002	CH_3	F	CH_3	152-155
2.003	H	F	CH_2CH_3	
2.004	CH_3	F	CH_2CH_3	138-140
2.005	H	F	$(CH_2)_2CH_3$	
2.006	CH_3	F	$(CH_2)_2CH_3$	142-144
2.007	H	Cl	CH_3	222-225
2.008	CH_3	Cl	CH_3	
2.009	H	Cl	CH_2CH_3	185-188
2.010	CH_3	Cl	CH_2CH_3	
2.011	H	Cl	$(CH_2)_2CH_3$	
2.012	CH_3	Cl	$(CH_2)_2CH_3$	
2.013	H	Br	CH_3	220-225 (decomp.) 185 (decomp.) sodium salt
2.014	CH_3	Br	CH_3	
2.015	H	Br	CH_2CH_3	
2.016	CH_3	Br	CH_2CH_3	
2.017	H	Br	$(CH_2)_2CH_3$	
2.018	CH_3	Br	$(CH_2)_2CH_3$	
2.019	H	Cl	$CH(CH_3)_2$	
2.020	CH_3	Cl	$CH(CH_3)_2$	
2.021	H	F	$CH(CH_3)_2$	194-196
2.022	CH_3	F	$CH(CH_3)_2$	
2.023	H	F	$CH_2CH=CH_2$	
2.024	CH_3	F	$CH_2CH=CH_2$	
2.025	H	Cl	$CH_2CH=CH_2$	116-120
2.026	CH_3	Cl	$CH_2CH=CH_2$	
2.027	H	Cl	$(CH_2)_2O(CH_2)_2Cl$	148-151 180 (decomp.) sodium salt
2.028	CH_3	Cl	$(CH_2)_2O(CH_2)_2Cl$	
2.029	H	F	$(CH_2)_2O(CH_2)_2Cl$	
2.030	CH_3	F	$(CH_2)_2O(CH_2)_2Cl$	

Table 3



No.	R^1	R^2	R^3	mp. (°C)
3.001	H	CH_3	H	148-151
3.002	CH_3	CH_3	H	116-118
3.003	H	CH_3	Cl	
3.004	CH_3	CH_3	Cl	
3.005	H	CH_2CH_3	H	
3.006	CH_3	CH_2CH_3	H	
3.007	H	CH_2CH_3	Cl	
3.008	CH_3	CH_2CH_3	Cl	
3.009	H	$(CH_2)_2CH_3$	H	
3.010	CH_3	$(CH_2)_2CH_3$	H	
3.011	H	$(CH_2)_2CH_3$	Cl	
3.012	CH_3	$(CH_2)_2CH_3$	Cl	
3.013	H	$CH(CH_3)_2$	H	
3.014	CH_3	$CH(CH_3)_2$	H	
3.015	H	$CH(CH_3)_2$	Cl	
3.016	CH_3	$CH(CH_3)_2$	Cl	
3.017	H	$(CH_2)_3CH_3$	H	
3.018	CH_3	$(CH_2)_3CH_3$	H	
3.019	H	$(CH_2)_3CH_3$	Cl	
3.020	CH_3	$(CH_2)_3CH_3$	Cl	

Table 4



No.	R1	R2	R3	R4	R5	mp. (°C)
4.001	H	CH_3	H	CH_3	H	
4.002	CH_3	CH_3	H	CH_3	H	
4.003	H	CH_2CH_3	H	CH_3	H	
4.004	CH_3	CH_2CH_3	H	CH_3	H	
4.005	H	$(CH_2)_2CH_3$	H	CH_3	H	
4.006	CH_3	$(CH_2)_2CH_3$	H	CH_3	H	
4.007	H	CH_3	F	CH_3	H	
4.008	CH_3	CH_3	F	CH_3	H	
4.009	H	CH_3	F	CH_3	CH_3	178-179 192(decomp.) [sodium salt]
4.010	CH_3	CH_3	F	CH_3	CH_3	
4.011	H	CH_3	Cl	CH_3	H	
4.012	CH_3	CH_3	Cl	CH_3	H	
4.013	H	CH_3	Cl	CH_3	CH_3	
4.014	CH_3	CH_3	Cl	CH_3	CH_3	
4.015	H	CH_3	Br	CH_3	H	
4.016	CH_3	CH_3	Br	CH_3	H	
4.017	H	CH_3	Br	CH_3	CH_3	
4.018	CH_3	CH_3	Br	CH_3	CH_3	
4.019	H	CH_3	H	CH_3	CH_3	
4.020	CH_3	CH_3	H	CH_3	CH_3	
4.021	H	CH_3	H	CH_2CH_3	H	
4.022	CH_3	CH_3	H	CH_2CH_3	H	
4.023	H	CH_3	H	$(CH_2)_2CH_3$	H	
4.024	CH_3	CH_3	H	$(CH_2)_2CH_3$	H	
4.025	H	CH_3	H	$CH(CH_3)_2$	H	
4.026	CH_3	CH_3	H	$CH(CH_3)_2$	H	
4.027	H	CH_3	F	CH_2CH_3	H	
4.028	CH_3	CH_3	F	CH_2CH_3	H	
4.029	H	CH_3	F	$(CH_2)_2CH_3$	H	
4.030	CH_3	CH_3	F	$(CH_2)_2CH_3$	H	
4.031	H	CH_3	F	$CH(CH_3)_2$	H	
4.032	CH_3	CH_3	F	$CH(CH_3)_2$	H	

Table 4 (contd.)

No.	R^1	R^2	R^3	R^4	R^5	mp. (°C)
4.033	H	CH_3	Cl	CH_2CH_3	H	
4.034	CH_3	CH_3	Cl	CH_2CH_3	H	
4.035	H	CH_3	Cl	$(CH_2)_2CH_3$	H	
4.036	CH_3	CH_3	Cl	$(CH_2)_2CH_3$	H	
4.037	H	CH_3	Cl	$CH(CH_3)_2$	H	
4.038	CH_3	CH_3	Cl	$CH(CH_3)_2$	H	
4.039	H	CH_3	H	CH_2CH_3	CH_3	
4.040	CH_3	CH_3	H	CH_2CH_3	CH_3	
4.041	H	CH_3	H	CH_2CH_3	CH_2CH_3	
4.042	H	CH_3	F	CH_2CH_3	CH_2CH_3	
4.043	H	CH_3	H	$(CH_2)_2CH_3$	$(CH_2)_2CH_3$	
4.044	H	CH_3	F	$(CH_2)_2CH_3$	$(CH_2)_2CH_3$	
4.045	H	CH_3	H	$(CH_2)_3CH_3$	$(CH_2)_3CH_3$	
4.046	H	CH_3	F	$(CH_2)_3CH_3$	$(CH_2)_3CH_3$	
4.047	H	CH_3	H	$(CH_2)_2OCH_3$	H	
4.048	H	CH_3	F	$(CH_2)_2OCH_3$	H	
4.049	H	CH_3	H	$(CH_2)_2OCH_3$	CH_3	
4.050	H	CH_3	F	$(CH_2)_2OCH_3$	CH_3	
4.051	H	CH_3	H	$CH_2CH=CH_2$	H	
4.052	H	CH_3	F	$CH_2CH=CH_2$	H	
4.053	H	CH_3	H	$CH_2CH=CH_2$	CH_3	
4.054	H	CH_3	F	$CH_2CH=CH_2$	CH_3	
4.055	H	CH_3	H	$(CH_2)_2O(CH_2)_2OCH_3$	H	
4.056	H	CH_3	F	$(CH_2)_2O(CH_2)_2OCH_3$	H	
4.057	H	CH_3	H	$-(CH_2)_4-$		
4.058	H	CH_3	F	$-(CH_2)_4-$		
4.059	CH_3	CH_3	H	$-(CH_2)_4-$		
4.060	CH_3	CH_3	F	$-(CH_2)_4-$		
4.061	H	CH_3	H	$-(CH_2)_5-$		
4.062	CH_3	CH_3	H	$-(CH_2)_5-$		
4.063	H	CH_3	F	$-(CH_2)_5-$		
4.064	CH_3	CH_3	F	$-(CH_2)_5-$		
4.065	H	CH_3	H	$-(CH_2)_6-$		
4.066	CH_3	CH_3	H	$-(CH_2)_6-$		
4.067	H	CH_3	F	$-(CH_2)_6-$		
4.068	CH_3	CH_3	F	$-(CH_2)_6-$		
4.069	H	CH_3	H	$-(CH_2)_2O(CH_2)_2-$		
4.070	CH_3	CH_3	H	$-(CH_2)_2O(CH_2)_2-$		
4.071	H	CH_3	F	$-(CH_2)_2O(CH_2)_2-$		

Table 4 (contd.)

No.	R^1	R^2	R^3	R^4	R^5	mp. (°C)
4.072	CH_3	CH_3	F		$-(CH_2)_2O(CH_2)_2-$	
4.073	H	CH_3	H		$-(CH_2)_2NCH_3(CH_2)_2-$	
4.074	CH_3	CH_3	H		$-(CH_2)_2NCH_3(CH_2)_2-$	
4.075	H	CH_3	F		$-(CH_2)_2NCH_3(CH_2)_2-$	
4.076	CH_3	CH_3	F		$-(CH_2)_2NCH_3(CH_2)_2-$	

Use examples:

The herbicidal action of sulfonylureas of the formula I on the growth of the test plants is demonstrated by the following greenhouse experiments.

The vessels employed were plastic flowerpots having a volume of 300 cm^3 and filled with a sandy loam containing about 3.0% humus. The seeds of the test plants were sown separately, according to species.

For the postemergence treatment, either plants sown directly in the pots and grown there were used, or plants which were cultivated separately as seedlings and were transplanted to the vessels a few days before treatment.

Depending on growth form, the plants were grown to a height of 3 to 15 cm before being treated with the active ingredients, which were suspended or emulsified in water and sprayed through finely distributing nozzles. The application rate for postemergence treatment was 0.125 kg/ha.

The pots were set up in the greenhouse, species from warmer climates in warmer areas (20 to 35°C) and species from moderate climates at 10 to 20°C. The experiments were run for from 2 to 4 weeks. During this time the plants were tended and their reactions to the various treatments assessed.

The assessment scale was 0 to 100, 100 denoting nonemergence or complete destruction of at least the visible plant parts, and 0 denoting no damage or normal growth.

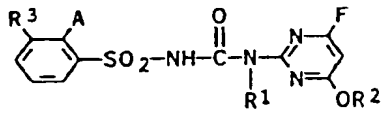
The plants used in the greenhouse experiments were Amaranthus retroflexus, Brassica napus, Chrysanthemum corinarium, Cyperus esculentus, Echinochloa crus-galli, Malva neglecta, Matricaria inodora, Sinapis alba, Solanum nigrum, Stellaria media, Veronica spp. and Triticum aestivum.

The compound of Example 1.001, applied pre- or postemergence at a rate of 0.125 kg/ha, gives excellent control of unwanted plants.

Compounds 1.009, 1.058 and 1.059, applied at a rate of 0.15 kg/ha, combat unwanted broadleaved plants very well without causing any appreciable damage to wheat as an example of a crop plant.

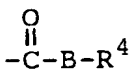
WHAT IS CLAIMED IS:

1. A substituted sulfonylurea of the general formula (I):

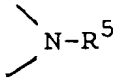


(I)

where R^1 is hydrogen, C_1-C_3-alkyl, C_3-C_6-alkenyl or C_3-C_6-alkynyl; R^2 is C_1-C_4-alkyl; R^3 is hydrogen or halogen, and A is halogen or a radical:



where B is oxygen or an alkylimino group:

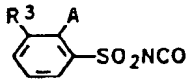


R^4 is hydrogen, C_1-C_6-alkyl which can carry up to three of the following: halogen, C_1-C_4-alkoxy, C_1-C_4-alkylthio, C_1-C_4-haloalkoxy, C_1-C_4-alkoxy-C_1-C_2-alkoxy, C_3-C_7-cycloalkyl and/or phenyl; C_5-C_7-cycloalkyl which can carry up to three C_1-C_4-alkyls; C_3-C_6-alkenyl or C_3-C_6-alkynyl, and R^5 is hydrogen, C_1-C_6-alkyl, or together with R^4 is a C_4-C_6-alkylene chain in which one methylene can be replaced by oxygen or C_1-C_4-alkylimino,
and environmentally compatible salts thereof.

2. A sulfonylurea of the formula (I) as set forth in claim 1, where R^1 is hydrogen or methyl, R^2 is C_1-C_4-alkyl, R^3 is hydrogen or halogen and A is $-CO_2R^4$, where R^4 is C_1-C_4-alkyl.

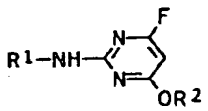
A

3. A process for the manufacture of a compound of the formula (I) as set forth in claim 1, A not denoting -COOH, wherein a sulfonylisocyanate II:



II

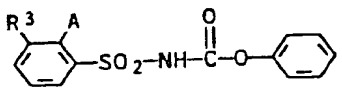
where R^3 is defined as in claim 1, is reacted in an inert organic solvent with an approximately stoichiometric amount of a 2-aminopyrimidine derivative III:



III

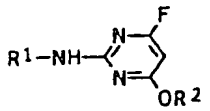
wherein R^1 and R^2 are defined as in claim 1.

4. A process for the manufacture of a compound of the formula (I) as set forth in claim 1, wherein a carbamate of the formula (IV):



IV

where R^3 is defined as in claim 1, is reacted in an inert organic solvent at from 0 to 120°C with an approximately stoichiometric amount of a 2-amino-pyrimidine III:

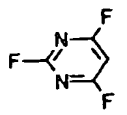


III

where R^1 and R^2 are defined as in claim 1.

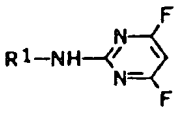
5. A process as claimed in claim 3 or 4, wherein the compound III is produced by reacting 2,4,6-trifluoropyrimidine (V):

A



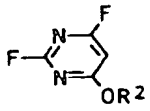
V

in an aprotic polar solvent in the presence of a base with an amine R^1NH_2 (VI) or with an amide R^1NHM^1 (VIa) where R^1 is defined as in claim 1 and M^1 is an alkali metal cation or one equivalent of an alkaline earth metal cation, at from -80 to +20°C to give a 2-amino-4,6-difluoropyrimidine VII



VII

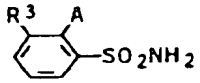
and then reacting this compound VII at 0 to 140°C in the presence or absence of a base with an alcohol R^2OH (VIII) or with an alcoholate R^2OM^1 (VIIIa) where R^2 is defined as in claim 1 to give the requested compound III, or by converting the compound V initially with the alcohol VIII or the alcoholate VIIIa to form the ether IX:



IX

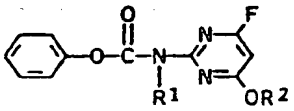
and then reacting this ether with VI or VIa to give the requested compound III.

6. A process for the manufacture of a sulfonylurea of the formula I as set forth in claim 1, wherein a corresponding sulfonamide of the formula X:



X

where R^3 and A are defined as in claim 1 is reacted in an inert organic solvent with a phenylcarbamate XI:



XI

where R^1 and R^2 are defined as in claim 1.

7. A herbicidal agent containing a sulfonylurea of the formula I as set forth in claim 1, or a salt thereof, and a conventional carrier therefor.

8. A process for combating the growth of unwanted plants, wherein a herbicidally effective amount of a sulfonylurea of the formula (I) as set forth in claim 1, or a salt thereof, is allowed to act on the plants and/or their habitat.

9. A process for combating the growth of unwanted plants in Indian corn, wherein a herbicidally effective amount of methyl 2-[[(4-fluoro-6-methoxy-1,3-pyrimidin-2-yl)aminocarbonyl) aminosulfonyl]-benzoate is used.

10. The use of a compound of the formula (I) as set forth in claim 1 as a herbicidal agent.

11. The use of methyl 2-[(4-fluoro-6-methoxy-1,3-pyrimidin-2-yl)amino-carbonyl]aminosulfonyl]benzoate as a herbicidal agent in Indian corn.

12. A process for regulating the plant growth, wherein a growth-regulating amount of a sulfonylurea of the formula I as set forth in claim 1, or a salt thereof, is allowed to act on the seed, the plants and/or their habitat.

A